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Document Name: ASTM E168: Standard Practices for General Techniques of Infrared Quantitative Analysis

CFR Section(s): 40 CFR 60.485(d)(1)

Standards Body: American Society for Testing and Materials

APPROVED

Official Incorporator:
THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: E 168 – 67

Standard Recommended Practices for
GENERAL TECHNIQUES OF INFRARED QUANTITATIVE ANALYSIS[1]

This Standard is issued under the fixed designation E 168; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 These recommended practices cover the various techniques most often used in infrared quantitative analysis. The purpose is to render unnecessary the repetition of these descriptions of techniques in individual methods for infrared quantitative analysis.

NOTE 1—The values stated in U.S. customary units are to be regarded as the standard. The metric equivalents of U.S. customary units may be approximate.

2. Definitions and Symbols

2.1 For definitions of terms and symbols, refer to ASTM Definitions E 131, Terms and Symbols Relating to Molecular Spectroscopy.[2]

3. Theory

3.1 Quantitative spectrophotometry is based on Beer-Bouguer's law (**7,11**)[3] which may be expressed in the following form when applied to a mixture of n independently absorbing components:

$$A_\lambda = a_1bc_1 + a_2bc_2 + \cdots + a_nbc_n \qquad (1)$$

where:

A_λ = absorbance (total) of the sample at the wavelength, λ,
a_j = absorptivity of component j at the wavelength, $\lambda (j = 1, 2, \cdots n)$,
c_j = concentration of component j, and
b = sample path length.

A total of n wavelengths is chosen, each characteristic of one of the n components. These choices are governed by compromises between sensitivity and freedom from interfering absorption. Rewriting Eq 1 for each of these n wavelengths yields a set of n equations:

$$\begin{aligned} A_1 &= a_{11}b_1c_1 + a_{12}b_1c_2 + \ldots + a_{1n}b_1c_n \\ A_2 &= a_{21}b_2c_1 + a_{22}b_2c_2 + \cdots + a_{2n}b_2c_n \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ A_n &= a_{n1}b_nc_1 + a_{n2}b_nc_2 + \ldots + a_{nn}b_nc_n \end{aligned} \qquad (2)$$

The values of A_i, the absorbance at wavelength λ_i, are determined for a sample of the mixture, the values of a_{ij} (absorptivity at wavelength i of component j) are determined from measurement of synthetic mixtures of these components or of the pure individual components (see Section 8) and the values of b_i are the known sample path lengths. The n equations of Eq 2 can therefore be solved for the n unknown concentrations, c_j.

3.2 When a single, fixed sample path length is employed both for calibration and for analysis, it is not necessary to measure the sample path length explicitly. The absorptivity-sample path length product, $a_{ij}b_i$, may be treated as one coefficient and could be replaced in Eq 2 by the term α_{ij}. This combined coefficient is determined from measurement of mixtures of the pure individual components in the analytical cell (see Section 8). Because changes in cell thickness will cause corresponding changes in the numerical value of α_{ij}, the cell thickness should be determined periodically by the procedure given in ASTM Recommended Practice E 275, for Describing and Measuring Performance of Spectrophotometers.[2] When significant changes in the cell path length are observed, corresponding corrections can be made to the value of α_{ij}.

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[1] These recommended practices are under the jurisdiction of ASTM Committee E-13 on Molecular Spectroscopy.

Current edition effective Sept. 8, 1967. Originally issued 1960. Replaces E 168 – 64 T.

[2] *Annual Book of ASTM Standards*, Part 30.

[3] The boldface numbers in parentheses refer to the references listed at the end of these recommended practices.

4. Apparatus

4.1 Refer to Recommended Practice E 275. However, the technique descriptions given here assume only that the equipment is of the usual commercial quality.

5. Sample Preparation

5.1 *Gaseous Samples*—Prepare gases for analysis by filling an appropriate gas cell. This is usually most conveniently done by the use of a vacuum system. Predetermine the proper sample concentration by establishment of the sample path length, the partial pressure of the sample, and the total cell pressure (including provision for the addition of any diluent gas) to be employed in analysis.

NOTE 2—All measurements for calibration and analysis under a given analytical system should be made at a single, reproducible total pressure.

5.2 *Liquids*—Determine infrared spectra of liquids and of low melting-point solids on the samples in their liquid form in a cell (or heated cell at a specified temperature) of suitable thickness (**1,6**).

5.3 *Dissolution Techniques*—Handle liquid and solid samples in solution by one of the following procedures:

5.3.1 Choose a solvent which does not absorb at the analytical wavelengths.

5.3.2 Weigh a specified amount of sample into a suitable volumetric flask.

5.3.3 Add most of the solvent and shake to dissolve the sample completely.

5.3.4 Make up to volume with solvent and mix thoroughly (solvent and flask should be at approximately the same temperature as the spectrophotometer).

NOTE 3—Solvent influences on the absorptions to be measured must be absent or known.

5.4 *Solids by Mull Techniques* (**3**):

5.4.1 Weigh slightly more than the minimum amount of sample required, and then weigh the desired ratio of an appropriate internal standard. Mix together in a smooth agate mortar.

5.4.2 Break up the mixture and distribute it over the mortar surface by gentle grinding with an agate pestle.

5.4.3 Rub to an extremely fine powder by vigorous back and forth grinding until the mixture becomes caked and takes on a smooth, glassy surface reflecting to light.

5.4.4 Add mulling agent[4] dropwise, grinding with a rotary motion until all of the mixture is picked up and suspended (the suspension should be viscous, not fluid).

5.4.5 Transfer the sample to a flat salt plate with a rubber policeman.

5.4.6 Cover with a second flat plate, squeeze and rotate to obtain the desired thickness.

NOTE 4—Particle size of the sample should be reduced to an order of magnitude less than the analytical wavelength. This is relatively easy for many samples without incurring any change in the sample. However, polymorphic changes, degradation, and other changes may occur during grinding.

5.5 *Solids by Pressed Pellet Technique* (**4,12**):

5.5.1 Hand grind the sample to an extremely fine powder, using an agate mortar and pestle. Grinding conditions must be established for the particular sample type since grinding severity can affect absorption band intensity.

NOTE 5—It is often advantageous when grinding the sample to use a few drops of absolute methanol or ethanol.

5.5.2 Weigh the preground sample and powdered potassium bromide in specified amounts and mix by hand in a mortar or with a grinder-mixer. This should be a mixing step and not a grinding step.

NOTE 6—If a grinder-mixer is used, stainless-steel vials and balls are recommended.

5.5.3 Place the mixture in an appropriate die and press at sufficient pressure (60,000 to 100,000 psi (4200 to 7000 kgf/cm^2)) to produce a transparent disk.

NOTE 7—Under these conditions, some samples may undergo chemical reaction with potassium bromide.

6. Analytical Wavelengths

6.1 For best accuracy, an analytical wavelength, λ_i, for the determination of component j, is chosen where component j has highest absorptivity in proportion to the combined absorptivities of the other components.

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[4] Nujol, Fluorolube, or equivalent has been found satisfactory for this purpose.

6.2 Analytical wavelengths should be chosen to give absorbance values which fall within the acceptable accurate range of the particular spectrophotometer used. In addition to wavelength selection, variation of concentration and of sample path length may be employed to meet this condition.

7. Absorbance Measurement

7.1 *Point Method:*

7.1.1 Set the instrument at the analytical wavelength, and with the sample cell and sample in the beam, read the transmitted radiant power, P_1.

7.1.2 With all instrument settings the same, read transmitted radiant power, P_2, according to one of the following conditions:

7.1.2.1 If the sample is in vapor form, remove the sample by pumping, and with the empty cell in the beam, read radiant power, P_2.

7.1.2.2 If the sample is in solution, replace the sample solution with pure solvent in the sample cell and read P_2.

7.1.2.3 If the sample is in liquid form, an alternative procedure is to replace the sample cell with a single plate of the same window material as used in the cell and read P_2. In this case, a correction constant may be required.

7.1.3 When taking the radiant-power readings, the subtraction of a zero reading from the transmitted power readings is usually required. This zero reading, P_3, is best obtained by band bottoming. In this procedure, radiant energy is measured as transmitted by a suitable thickness of a compound known to be opaque to the analytical wavelength radiant energy, but transparent to short wavelength scattered radiant energy. Lithium fluoride (LiF), calcium fluoride (CaF_2), or barium fluoride (BaF_2) are frequently used.

Transmitted radiant power, $P = P_1 - P_3$
Incident radiant power, $P_0 = P_2 - P_3$
Absorbance, $A = \log_{10} P_0/P$

NOTE 8—*Scanning*—The absorbance can be measured from scanned records where the same spectral interval is recorded under conditions of 7.1.1, 7.1.2, and 7.1.3.

NOTE 9—*Double-Beam Instruments* (**8**)—This procedure applies directly to readings on single-beam instruments which measure radiant power. Double-beam instruments read transmittance, T (or a function of transmittance), which is the ratio of the radiant power transmitted by a sample in the sample beam to the radiant power transmitted by a clearly specified reference material in the reference beam. If a double-beam instrument is employed, the reference beam should contain a carefully selected, reproducible reference material corresponding to that used in obtaining P_2 in 7.1.2. Calculations are then made substituting transmittance readings for corresponding radiant-power readings, P.

NOTE 10—*Direct Reading of Absorbance*—On some instruments an electrical network is provided that permits direct reading of the absorbance. In this case, complete Steps *2* and *3* (see 7.1.2 and 7.1.3) by setting the absorbance dial to read zero and adjusting the balancing dial until the indicator reads zero. Adjust the indicator independently to zero as in 7.1.3, with a radiation shutter in the beam and the absorbance dial set at infinity. Then carry out Step (*1*) (see 7.1.1) and obtain the reading by adjusting the absorbance dial until the indicator again reads zero. Read the absorbance of the sample directly. Specific instructions for commercial instruments are provided in the manufacturers' manuals.

7.2 *Baseline Method* (**5**)—This method ordinarily applies to scanned spectra, recorded either by single- or double-beam spectrophotometers. It consists of the following steps:

7.2.1 Record an interval of the spectrum containing the band to be measured. To establish the end points of the baseline, it is useful to rescan the interval with the sample removed from the beam (curve *B*, Fig. 1). It will be assumed that the zero is known.

7.2.2 Select two wavelengths, λ_1 and λ_2 (Fig. 1) at each side of the band to be measured, at which points the transmitted radiant power is as near as possible to curve *B* (Fig. 1). These points, λ_1 and λ_2, should be as free as possible of absorption by all components of the sample. Draw a straight line between the two selected points. This should be tangent to the spectrum curve at the two points and should be roughly parallel to curve *B*.

7.2.3 The values of P_0 and P are obtained as indicated in Fig. 1, and the absorbance is given by:

$$A = \log_{10} (P_0/P)$$

The same end points, λ_1 and λ_2, of the baseline are used on all subsequent absorbance measurements.

NOTE 11—After the end points are established, it is possible to use the baseline method using fixed-point readings; that is, without scanning. For this procedure, readings are taken at λ_1, λ, and λ_2. Incident radiant power, P_0, is calculated as a weighted average of readings at λ_1 and λ_2, and P is read directly at λ. P_0 may be calculated from a linear interpolation formula as follows:

$$P_0 = P_{\lambda 1} + (P_{\lambda 2} - P_{\lambda 1})[(\lambda - \lambda_1)/(\lambda_2 - \lambda_1)]$$

where:

$P_{\lambda 1}$ = the radiant power measured at λ_1,
$P_{\lambda 2}$ = the radiant power measured at λ_2, and
P_0 = a baseline incident radiant power at λ.

8. Analytical Curve Preparation

8.1 Quantitative spectrophotometry is based on Beer-Bouguer's law, which, for a mixture, takes the form of Eq 2 (see Section 3). The absorptivities, a_{ij}, of the various components, j, of the mixture at the wavelengths, i, selected for the analysis must be determined from absorbance measurements made on each component taken individually. These must be measured under conditions (sample path length, pressure, solvent), identical with those which will apply when the unknown is measured. Absorbance measurements should be made with concentrations of the component bracketing the amounts expected in the samples to be analyzed. Customarily, absorbances are plotted as ordinates versus the quantity of component as abscissa. This is the Beer-Bouguer law plot or analytical curve. Component quantity is usually expressed as a partial pressure or mole fraction, if a gas, and as a concentration in grams per liter or as a weight fraction if a liquid or solid. This plot, to a first approximation, is a straight line passing through the origin, the slope of which is the value of the product, $a_{ij}b_i$. Treatment of the case where the plot has appreciable curvature is described in 9.4.

8.1.1 *Gases*—All calibration measurements for a given analysis must be made at a fixed total pressure. This pressure must be equal to the total pressure employed for analysis. Any given analysis may be set up in one of two methods: (*1*) a fixed sample pressure is used as the total pressure, or, preferably, (*2*) a fixed sample pressure is established which is a fraction of a total pressure attained by the addition of a nonabsorbing diluent gas. Analytical curves are prepared by introducing a pure component at various measured pressures which bracket the expected component pressures in the samples. A diluent gas is then added to bring the total pressure up to the established value. In method (*1*), the analytical curve prepared does not allow for the possible variation of band broadening for different components. This factor is more properly allowed for through a procedure following method (*2*) where the same diluent gas is employed for sample preparation and calibration. Absorbances are measured for each standard at the wavelengths selected for analysis. The absorbances are plotted against the partial pressures (or mole fractions) to produce the analytical curves.

8.1.2 *Solutions*—Where possible, samples should be run as dilute solutions in thick cells (0.5 to 1.0 mm) in preference to running as more concentrated solutions in thin cells. In this manner, percentage composition ranges over which a linear relationship is attained can be extended considerably. At the same time, this approach will minimize intermolecular effects. Where freedom from intermolecular effects is uncertain or where intermolecular effects are known to be present, calibration must be based on measurements taken from synthetic mixtures of all the components as described in 8.1.3.

8.1.2.1 When a given analytical system is known to be free of intermolecular effects, one pure component is introduced into the cell at a known concentration in a nonabsorbing solvent (preferably carbon disulfide (CS_2) or carbon tetrachloride (CCl_4)). The absorbance at the selected wavelength is then measured and plotted against concentration. Several such points are plotted covering the range of concentrations expected in the samples to be analyzed. Similarly, analytical plots are constructed for this component at each of the other analytical wavelengths to be used in the analysis of the given mixture. This procedure is repeated for each of the n components. Thus, there are n plots for each component, or a total of n^2 analytical curves, each yielding one of the values of $a_{ij}b_i$.

8.1.3 *Liquids*—Analyzing a liquid mixture without the use of a diluting solvent is sometimes complicated by intermolecular forces. An absorption band may undergo intensity or wavelength changes, or both, when the component is in solution. The absorbance contribution of a component in a mixture can seldom be calculated from its absorbance measured in the pure state. It is necessary to determine the absorptivities from known mixtures having proportions near those of the samples. The following procedure is probably most straightforward.

8.1.3.1 Prepare standard mixtures having concentrations of the various components covering the range to be expected in the samples. Measure absorbances at each of the wavelengths chosen for the analysis and substitute them (along with the known concentrations) into Beer-Bouguer law equations (Eq 2), which may then be solved for the absorptivity-sample path length products, $a_{ij}b_i$. The number of standard mixtures required is equal to n, the number of components to be determined. For each analytical wavelength there will be a set of n equations in n unknowns. The n sets of these equations can be solved individually for the values of $a_{ij}b_i$. It is recommended that more than n synthetic mixtures be prepared, and that least squares procedures be used to calculate all values of $a_{ij}b_i$ (or α_{ij}).

8.1.3.2 Because of the intermolecular influences, it is recommended that the calculation of the absorptivity-sample path length products be repeated using a second set of n standard mixtures if the concentrations in the unknowns vary widely. The differences in the values of the absorptivities thus determined will indicate the extent of intermolecular influences. It may not be possible to analyze mixtures throughout all possible concentration ranges of the components using a single set of absorptivities. Since the absorptivity-sample path length products are calculated directly in this procedure, it is not necessary to plot analytical curves.

8.1.3.3 It may be possible, as an alternative procedure, to prepare standard mixtures containing only two components at a time. This reduces the problem to a series of sets of two simultaneous equations in two unknowns. However, all possible combinations are required to evaluate the intermolecular effects. It is also not possible in a two-component standard mixture to have both concentrations near those of the average sample to be analyzed.

8.1.4 *Solids*—For solids in film form, follow the same general procedure as for liquids, see 8.1.3. Measure the thickness of each film and apply a proportional correction for deviation from standard thickness. Baseline absorbance measurements are normally employed.

8.1.4.1 In cases where all components of a mixture are determined to a total of 100 percent, it is usually sufficient to know only the ratios of absorptivities. In such cases it is not necessary to know the thickness of the sample layer.

8.1.4.2 The same procedure as for films may be used with powders in the form of mulls. Measurement of thickness can be accomplished by an internal standard technique. This involves the addition to the sample of a known weight ratio of a compound having an absorption band of known absorptivity that does not overlap the bands of the sample. Again, where the components measured must total 100 percent, it is not necessary to measure thickness.

8.1.4.3 When powders are measured as pressed plates or pellets, analytical curves can ordinarily be prepared in the same manner as for solutions, see 8.1.2.

9. Calculation Methods

9.1 *Matrix Inversion* (**10**)—After the values of the absorptivity-sample path length products have been determined for a given set of components, substitute the numerical values into the Beer-Bouguer law equations (Eq 2). These equations are then solved for the concentrations, c_j, in terms of the absorbances, A_i. This is known as matrix inversion. The solved (or inverted) equations will have the form:

$$\begin{aligned} c_1 &= A_1F_{11} + A_2F_{12} + \cdots + A_nF_{1n} \\ c_2 &= A_1F_{21} + A_2F_{22} + \cdots + A_nF_{2n} \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ c_n &= A_1F_{n1} + A_2F_{n2} + \dots + A_nF_{nn} \end{aligned} \quad (3)$$

where F_{ji} will be known numbers. Thereafter calculation of individual sample concentration is simply done by substituting the measured absorbance values, A_i, in these equations.

9.2 *Successive Approximation*—The Beer-Bouguer law equations may be solved for each individual sample of a multicomponent mixture. In this case, the known values of a_{ii}, and the measured absorbances, A_i, are substituted into the Beer-Bouguer law equations. These equations are solved by a method of successive approximation as follows, taking a four-component mixture as example.

$$A_1 = \alpha_{11}c_1 + \alpha_{12}c_2 + \alpha_{13}c_3 + \alpha_{14}c_4 \quad (4)$$

$$A_2 = \alpha_{21}c_1 + \alpha_{22}c_2 + \alpha_{23}c_3 + \alpha_{24}c_4 \quad (5)$$

$$A_3 = \alpha_{31}c_1 + \alpha_{32}c_2 + \alpha_{33}c_3 + \alpha_{34}c_4 \quad (6)$$

$$A_4 = \alpha_{41}c_1 + \alpha_{42}c_2 + \alpha_{43}c_3 + \alpha_{44}c_4 \quad (7)$$

All numbers in Eqs 4 through 7 are known except the values of c_j.

9.2.1 *First Approximation:*

$$c_2 = A_2/\alpha_{22}, \quad c_3 = A_3/\alpha_{33}, \quad c_4 = A_4/\alpha_{44}$$

9.2.2 *Second Approximation:*

9.2.2.1 Substitute the first approximation values for c_2, c_3, and c_4 in Eq 4 and solve for c_1. This value is the second approximation for c_1.

9.2.2.2 Substitute the second approximation value for c_1 and the first approximation values for c_3 and c_4 into Eq 5. Solution of this equation gives the second approximation value for c_2.

9.2.2.3 Substitute the second approximation values for c_1 and c_2 and the first approximation value for c_4 into Eq 6. Solution of this equation gives the second approximation value for c_3.

9.2.2.4 Substitute the second approximation values for c_1, c_2, and c_3 into Eq 7 and solve for the second approximation value of c_4.

9.2.3 *Intermediate Approximations:*

9.2.3.1 Employing the c_j values obtained in the preceding approximation, obtain each successive set of approximate values as described in the above procedure for obtaining the second approximation.

9.2.4 *Final Solution:*

9.2.4.1 Repeat the determination of higher approximations until there is no significant change in values.

9.3 *Graphical*—A successive approximation method equivalent to that described in 9.2 can be carried out graphically where analytical curves have been prepared. For n components there will be a set of n Beer-Bouguer law plots drawn for each of the n analytical wavelengths.

9.3.1 In this case first-approximation values are determined from component analytical curves. These values are then used to determine absorbance contributions at each wavelength. These absorbance contributions are subtracted from the measured absorbance value for each constituent in turn. Each constituent is reevaluated using the most recent approximate value for the concentrations of all other components. This process is repeated until no further changes take place in the values calculated for c_j.

9.4 *Correction for Curvature of Beer-Bouguer Law Plots*—In some cases the Beer-Bouguer law plots of one or more components of a mixture will exhibit curvature to such an extent that the value of the slope may differ appreciably between low and high concentrations. If the graphical method (see 9.3) is used, no change in procedure is required. If the concentrations of such components in the samples to be analyzed fall in the low range, it is permissible to use the value of the slope for this low range without any correction to the above methods of calculation (see 9.1 and 9.2). However, if the concentration is larger, it is necessary to apply a correction. The following method is recommended:

9.4.1 The concentration of the component under consideration ranges in the sample between c_1 and c_2, Fig. 2. Draw a straight line between A_1 and A_2 (or the straight line approximating the curve between A_1 and A_2 most closely). The slope of this line is the absorptivity-sample path length product that is to be used in the Bouguer-law equations. The intercept of this line with the absorbance axis yields the value, A_0, of a correction term which must be subtracted from the measured absorbance of the sample at the analytical wavelength of the component. $A - A_0$ is substituted for A in the Beer-Bouguer law equation for this analytical wavelength. If the concentration of the component under consideration should happen to fall considerably outside the range c_1 to c_2, it will be necessary to repeat the above procedure to determine the slope and intercept for the new concentration range.

10. Special Techniques

10.1 *Reference Standard Method*—This method can be regarded as a special case of the point method of absorbance measurement. A known mixture or reference standard is used in 7.1.2 instead of pure solvent, empty, or dummy cell. The standard material used for reference should be as nearly identical to the average composition of the samples being measured as possible. The reference standard is usually measured in the same cell as the sample.

10.1.1 The value of log P_0/P thus obtained is the difference between sample absorbance and reference-standard absorbance and may be either negative or positive. The measured difference is then added (algebraically) to the known absorbance of the reference standard to obtain the absorbance of the sample.

NOTE 12—This method is usually expected to yield high accuracy as it allows a nearly null comparison of sample and standard and does not require intervening measurement of the total incident radiant power.

NOTE 13—The baseline method can also be applied in the reference standard procedure. Absorbances of sample and standard are obtained in quick succession. Here the nearly null comparison of sample and standard may also be expected to yield higher accuracy of absorbance measurement.

10.2 *Difference Method* (**9**)—In the difference method, the difference in the radiant power transmitted by a sample and a reference cell is measured directly by means of a double-beam spectrophotometer. This is illustrated in Fig. 3 for an ideal mixture which does not show solvent effects. Since the composition and absorbance of the material in the reference cell is known, the difference spectrum can be used to obtain the composition of the sample. The procedure may be identical with that of the reference standard method, see 10.1, except that thicker cells are usually employed in order to maximize the absorbance difference measured. However, the method is most often employed for partial rather than complete analysis. In these cases one of two principal procedures is employed, dependent on whether major or minor components are to be determined.

10.2.1 *Determination of Minor Components*—In this application, the reference cell is filled with the pure major component. The sample path length is chosen so that the amount of major component in the reference beam is the same as that in the sample beam. This may be accomplished most easily by using a variable path-length reference cell and adjusting its thickness so that the strongest bands of the major component are removed from the spectrum. The resulting spectrum of the minor components is then measured and interpreted quantitatively by the usual procedures. Analytical curves are prepared according to the procedure outlined in 8.1.2 for solutions, regarding the major component as the solvent. The baseline method described in 7.2 is usually used for absorbance measurements.

10.2.1.1 This method can be readily applied to solutions. The advantage of the difference technique is that the solvent or major component need not be transparent at the analytical wavelengths of the other components. It need only transmit sufficient radiant power at these analytical wavelengths to give a suitable detector response (**2**).

10.2.2 *Determination of Major Component*—In this case, reference and sample cells contain the component to be determined. The difference in absorbance between a sample and a reference standard is measured. The concentration is then determined from a calibration curve of difference measurements made for similar mixtures of known concentration. If interference from minor components at the analytical wavelength is small, the reference cell need only contain the major component. For maximum accuracy, minor constituents should also be present in the reference sample in approximately the same concentrations as occur in the sample being analyzed. The sample path length is chosen to give a sample absorbance in the range of 1.0 to 1.4 (higher absorbances give greater analytical sensitivity, provided adequate detector response is obtained). The reference path length is usually adjusted to give difference absorbance values in the range of 0.01 to 0.10.

10.2.2.1 Samples having two or more major components can also be analyzed by the difference method, using analytical curves or the calibration and calculation procedures described in 8.1.3 and Section 9. The data so obtained can then be used to prepare a synthetic blend of major components for use as a reference-cell sample in determining minor components in the sample.

10.2.3 *Method Using Variable Thickness Cell*—This method is applicable to gases, liquids, and solutions, and is advantageous in that no blank or dummy cells are required and that absorption by the cell need not be measured.

10.2.3.1 This method requires a cell which can be varied in thickness by at least a factor of two, and which provides accurate measurement of the difference in thickness between different settings. Absolute path length measurement is not required.

10.2.3.2 The method consists of plotting log

P at the analytical wavelength versus sample path-length readings. The incident radiant power, P_0, is held constant during these measurements, but its value does not enter into the calculation. This follows from Beer-Bouguer's law which states that at any wavelength:

$$\log (P_0/P) = abc + K$$

or

$$\log P = -abc - K + \log P_0$$

where K = the absorbance of the cell.

10.2.3.3 Plotting log P against the sample path length yields a straight line of which the negative slope is equal to ac. With a single component in the cell (or a single component in the common solvent), $c = 1$, and these plots yield the values of a_{ij}.

10.2.3.4 With the unknown mixture in the cell, plots of log P versus the sample path length reading are made at each of the n wavelengths chosen for the n components. The negative slopes of the lines plotted for each wavelength are the absorbances per unit of sample length and yield the following relations:

$$\begin{aligned} -\text{ slope at}_{\lambda 1} &= c_1a_{11} + c_2a_{21} + \cdots + c_na_{n1} \\ -\text{ slope at}_{\lambda 2} &= c_1a_{12} + c_2a_{22} + \ldots + c_na_{n2} \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ -\text{ slope at}_{\lambda n} &= c_1a_{1n} + c_2a_{2n} + \cdots + c_na_{nn} \end{aligned}$$

Since the values of a_{ij} are known, these equations may be solved in the usual manner for the concentrations.

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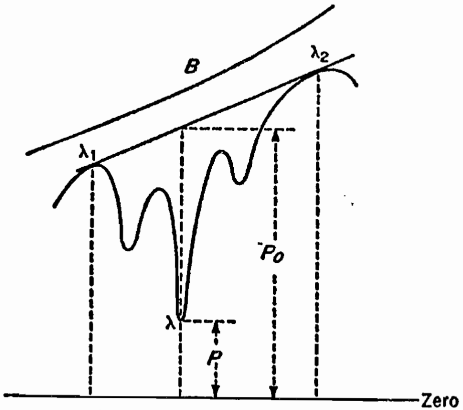


FIG. 1 Illustration of the Base-Line Method for Measuring Absorbance.

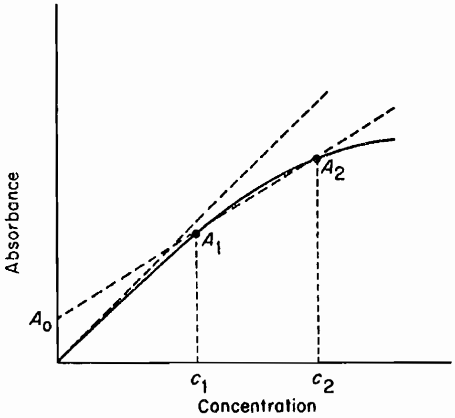
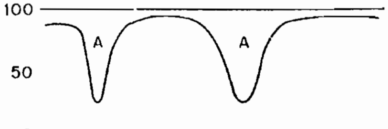
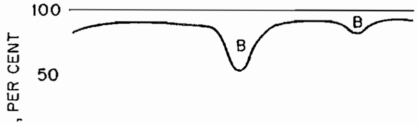


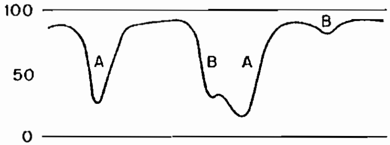
FIG. 2 Plot of Absorbance Versus Concentration.



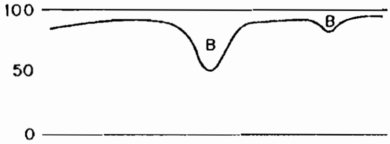
A–Transmission Spectrum of Compound A (Sample Thickness, a)



B–Transmission Spectrum of Compound B (Sample Thickness, b)



C–Transmission Spectrum of Mixture (A + B) (Sample Thickness, $a + b$)



D–Differential Spectrum Mixture (A + B) in Sample Beam (Sample Thickness $a + b$) Compound A in Reference Beam (Sample Thickness, a)

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FIG. 3 Illustration of Measurements by Difference Method.

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